Environmental Fate and Transport Modeling for Perfluorooctanoic Acid Emitted from the Washington Works Facility in West Virginia

Hyeong-Moo Shin,*[†] Verónica M. Vieira,[‡] P. Barry Ryan,[§] Russell Detwiler,[^] Brett Sanders,[^] Kyle Steenland,[§,||] and Scott M. Bartell[z]

[†]School of Social Ecology, [^]Department of Civil and Environmental Engineering, and [z]Program in Public Health, University of California, Irvine, California, United States
[‡]Department of Environmental Health, Boston University, Boston, Massachusetts, United States
[§]Department of Environmental Health, Emory University, Atlanta, Georgia, United States
[^]C8 Science Panel (http://www.c8sciencepanel.org)

ⓑ Supporting Information

ABSTRACT: Perfluorooctanoic acid (PFOA) has been detected in environmental samples in Ohio and West Virginia near the Washington Works Plant in Parkersburg, West Virginia. This paper describes retrospective fate and transport modeling of PFOA concentrations in local air, surface water, groundwater, and six municipal water systems based on estimates of historic emission rates from the facility, physicochemical properties of PFOA, and local geologic and meteorological data beginning in 1951. We linked several environmental fate and transport modeling systems to model PFOA air dispersion, transit through the vadose zone, surface water transport, and groundwater flow and transport. These include AERMOD, PRZM-3, BreZo, MODFLOW, and MT3DMS. Several thousand PFOA measurements in municipal well water have been collected in this region since 1998. Our linked modeling system performs better than expected, predicting water concentrations within a factor of 2.1 of the average observed water concentration for each of the six municipal water districts after adjusting the organic carbon partition coefficient to fit the observed data. After model calibration, the Spearman's rank correlation coefficient for predicted versus observed water concentrations is 0.87. These models may be useful for estimating past and future public well water PFOA concentrations in this region.

INTRODUCTION

The Washington Works Plant in West Virginia, owned and operated by the E.I. du Pont de Nemours Company (DuPont), has used ammonium perfluorooctanoate (APFO) in the manufacturing of fluoropolymers since 1951. APFO dissociates in water to form perfluorooctanoate (PFO$^-$) and ammonium ion (NH$_4^p$). Under acidic conditions, PFO$^-$ is protonated to form perfluorooctanoic acid (PFOA). PFO$^-$ and PFOA exist in different proportions in the environment depending on pH; reported pK$_a$ values for PFOA range from 0 to 3.8.[1-4] Although PFO$^-$ is a dominant species in the environment, we use the term "PFOA" here to be consistent with other literature. Historically PFOA was released from the facility through both stack and fugitive emissions that were carried by air currents and deposited on surfaces in the local area.[5] Further, liquid effluent containing PFOA has been released from the facility into the Ohio River. These emissions and releases have resulted in contamination of water supplies downwind and downstream from the facility.[5,6]

Studies with rats and mice found that PFOA caused the development of liver tumors[7,8] and might worsen fetal growth.[9,10] However, little is known in humans, mostly from occupational studies.[11] Individuals living or working in the region near the facility may have experienced PFOA exposures via particulate inhalation, water ingestion, local vegetable consumption, and dermal contact.[12] A series of epidemiologic studies are being conducted to determine if there is a probable link between PFOA

exposure to community residents and adverse health effects in the region surrounding the Washington Works facility.[13] Many of these studies include participants of the C8 Health Project, a cross-sectional study conducted from 2005 to 2006 that collected PFOA serum samples, residential histories, and other questionnaire responses from 69 030 individuals with past or current residence in the contaminated region.[14,15]

Estimated historical releases of PFOA from the facility are provided in the Supporting Information (Figure S1).[6] Emissions steadily increased since the 1950s and peaked around 2000. Control strategies have reduced emissions substantially since then.[16] Prevailing winds from the east and southwest preferentially carried the particulate form of PFOA to the west and northeast.[5,17] In addition, the Ohio River discharges have resulted in potential exposures downriver, essentially to the southwest. Exposure patterns within the contaminated region are likely to have varied substantially over space and time. The predominant historical exposure route for most nonoccupationally exposed individuals in this region is thought to be contaminated drinking water.[12,14,18] Although PFOA water concentrations during recent years are well characterized for a number of public water
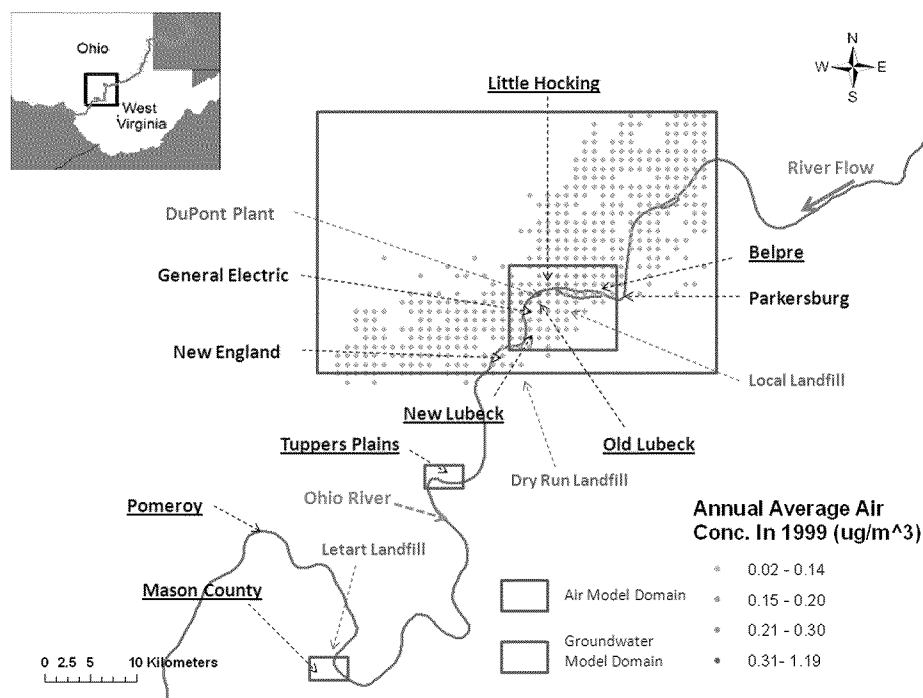
Figure 1. C8 Health Project study area, municipal water supply well locations, air model domain (green box), and groundwater model domain (red box).

districts in this region, reliable historical measurements are lacking.

Paustenbach et al. previously published a fate and transport model for PFOA emitted from this facility using mass balance estimates derived from purchasing and material use records and simplifying assumptions regarding several fate and transport model components.[6] We relied on the same emissions rate estimates, building configuration, and stack information. However, we used a different air dispersion model and applied advection-dispersion models for each model component rather than relying on well-mixed compartmental representations. The objective of our study is to estimate historical water PFOA concentrations in this region for eventual use in retrospective exposure estimates for a variety of epidemiologic analyses. Here we apply environmental fate and transport models to produce retrospective predictions for local air, surface water, and groundwater concentrations based on estimates of historic emission rates from the facility, physicochemical properties of PFOA, and local geologic and meteorological characteristics. Because many well water PFOA measurements are available for recent years (2000 - 2007), we calibrate our historical predictions to the recently observed water concentrations.

MATERIALS AND METHODS

Study Area. We applied environmental fate and transport models to the C8 Health Project study area (Figure 1), which encompasses six municipal water supplies whose customers were included in a legal settlement related to PFOA emissions from the Washington Works Plant.[14,15] Our model domains for air dispersion and groundwater modeling were chosen to include all six municipal water supplies and other areas with high particle deposition rates. The six municipal water supplies include the City of Belpre, Little Hocking Water Association, Tuppers Plains

Chester Water District, and Village of Pomeroy water district, located in Ohio, which started operating in 1955, 1969, 1969, and 1899, respectively. The Lubeck and Mason public service districts, located in West Virginia, started operating in 1960 and 1974, respectively. Of the six water districts, Belpre and Little Hocking wells are located upstream of the DuPont facility's primary aqueous discharging pipe and are thought to be contaminated via percolation of deposited PFOA through the soil after surface deposition.[5] Our air model domain (green box in Figure 1) is a large rectangular region encompassing four C8 Health Project public water supplies which are located downwind of the DuPont facility. Figure 1 also shows our predicted air concentrations from AERMOD (described in the Air Dispersion Model section of the Materials and Methods) for 1999, the year of peak air emissions from the facility, with levels ranging from 0 to 0.99 $\mu g/m^3$. Because the practical quantitation limit of PFOA in air is 0.14 $\mu g/m^3$,[19] nearly all measurable PFOA air concentrations due to the air emissions from the Washington Works facility should be captured within this model domain.[19]

The primary region for groundwater modeling (the large red box in Figure 1) was selected to include three municipal water supply wells requiring linked air - soil - surface water - groundwater models because of the transport of deposited PFOA through soil with rainfall recharge and the interaction of the contaminated Ohio River with groundwater. These municipal water supplies within the groundwater model wells include Belpre, Little Hocking, and Lubeck (with new and older well locations). Localized groundwater flow and transport models (the smaller red boxes in Figure 1) were also developed for the two downstream municipal water supply wells (Tuppers Plains and Mason County). Although these wells are far enough from the Washington Works facility that they are unlikely to have been influenced by aerial deposition of PFOA, their capture zones draw from both the Ohio River and saturated aquifers. PFOA

that was emitted to the Ohio River would have been drawn into these wells, but also diluted by simultaneous draw from uncontaminated groundwater. Finally, water concentrations for the Village of Pomeroy municipal water supply were assumed to be identical to Ohio River surface water concentrations at any point in time, because those wells draw primarily from the river located less than 50 m away.

Environmental Fate and Transport Models. Air emissions and liquid effluent from the facility to the Ohio River resulted in the contamination of surrounding environmental media including air, soil, and water. The primary sources of groundwater contamination are thought to be the infiltration of rainwater and groundwater recharge from the river, particularly in the vicinity of municipal well fields.[5] As the facility released PFOA through stacks, initially vapor phase emissions in the hot effluent gas coagulated under lower ambient temperatures and deposited on the ground surface overlying well fields by wet or dry deposition. Then, the deposited PFOA infiltrated through the vadose zone with rainfall recharge, eventually reaching the groundwater table. In addition, the cones of depression caused by pumping from wells adjacent to the river resulted in large hydraulic gradients between the river and pumping wells leading to significant flow of water from the Ohio River to groundwater pumping wells adjacent to the river. Scheme S1 in the Supporting Information depicts the conceptual framework explaining how the air, soil, surface water, and groundwater models are related to each other.

Air Dispersion Model. The American Meteorological Society/ EPA Regulatory Model (AERMOD) was used to estimate airborne PFOA concentrations and total deposition rates at geographical locations defined as receptors.[20] AERMOD has been EPA's preferred code for air dispersion modeling since December 2006. We also used ISC-AERMOD view, graphical interface software (Lakes Environmental, Waterloo, Ontario, Canada). The model contains the features of wet and dry deposition of airborne particles, building downwash effect, plume rise as a function of downwind distance, and terrain elevation effect. AERMOD was selected because it outperforms the U.S. EPA Industrial Source Complex Short-Term Version 3 (ISCST3)[21] on the prediction of ambient air concentrations and the deposition rates. The Barton et al. air modeling and monitoring study reported that AERMOD provided representative or conservative air concentration estimates for both off-site and on-site meteorological data.[17]

Most of the input parameters including building configuration, annual emission rates, and historical stack information applied in air dispersion modeling were obtained from Paustenbach et al.[6] Travel distance of particles is determined by particle size. Particles greater than 100 μm in diameter tend to deposit within 100 m of their point source.[22] Paustenbach et al.[6] collapsed the particle size data provided by DuPont into five particle size categories instead of using the measured categories of particle sizes. However, particle size was found to be the most influential parameter of the air dispersion model based on sensitivity analyses (unpublished data). Therefore, we used the particle size distributions from the direct measurements to avoid the possible loss of particle information from aggregation over multiple particle size categories. The model domain has a Cartesian grid array with a spacing of 200 m. Cartesian (X, Y) coordinates of the model origin are 401 000 and 4 318 000 m. Terrain elevation information was collected from WebGIS and assigned for each model grid point.[23]

Paustenbach et al. provided five years (1996, 1999 - 2002) of on-site preprocessed meteorological data which they used in

their ISCST3 air dispersion model. Due to the limited on-site meteorological data, we relied primarily on hourly recorded surface data from Parkersburg Airport (located 21 km northeast of the Washington Works facility) for the period of 1973 - 2008 and hourly precipitation data from Liverpool, WV (located about 40 - 50 km southeast of the Washington Works facility) prior to 1973.[24] Although most hourly recorded surface parameters including precipitation rate, temperature, mixing height, and roughness length have high correlations (0.8 - 0.95) between Parkersburg Airport and the 5 years of on-site data, wind direction and wind speed at the airport were not very representative of the facility site (correlations of 0.48 and 0.71, respectively). Primary on-site wind directions are to the northeast and west due to valley-driven flow, but winds at Parkersburg Airport flow more evenly in all directions. We therefore relied on the five years of on-site data to characterize wind speed and wind direction throughout 1951 - 2008, choosing the year with the closest total precipitation rate. Paustenbach et al. used a similar matching approach, but for all hourly surface parameters rather than just wind speed and wind direction.[6]

Vadose Zone Model. U.S. EPA Pesticide Root Zone Model Version 3 (PRZM-3), a one-dimensional, dynamic, compartmental model, was used to estimate surface soil concentration, subsurface soil concentration, storage in soil column, and the flux to groundwater.[25] The model was developed to evaluate the fate and transport of pesticides that are spread on agricultural surfaces. It models the penetration of such compounds from the surface through the vadose zone. We chose this model for its ability to simulate transport in soil, water movement, chemical runoff, and volatilization.

The PRZM-3 model, which we applied to the same domain as the main groundwater model, requires 22 physicochemical input parameters including bulk density, saturated hydraulic conductivity, organic carbon fraction, porosity, and longitudinal dispersivity.[25] These inputs, which are dependent on a soil type or a hydrologic soil group, are key parameters in estimating the fate and transport of PFOA in the vadose zone. Unlike the Paustenbach model, which defined modeling zones based on production-well capture zone and historical boundaries of water service districts regardless of dominant soil type, we assigned a dominant soil type to each model cell with a size of 400 m by 400 m by spatially joining the X and Y coordinates of the center of the cells to the soil shape file obtained from the State Soil Geographic (STATSGO) database of the U.S. Department of Agriculture (USDA) National Resource Conservation Service (NRCS).[26] We averaged the deposition rates of four 200 m by 200 m cells and assigned the average rate to one 400 m by 400 m cell. We applied the model independently in each grid block assuming that vertical PFOA transport via rainfall recharge from the surface through the vadose zone is independent across grid blocks (i.e., no lateral transport within the vadose zone). Due to limited vertical soil information, we assumed that the assigned soil type for each simulation cell is predominant vertically from the surface soil to the groundwater table. Another important parameter in estimating the transport of PFOA in the vadose zone is soil column thickness between ground surface and groundwater table. The groundwater elevation from the groundwater flow model developed by DuPont was used to calculate the soil column thickness by subtracting each cell head from each cell surface elevation.[27]

Surface Water Model. A depth-integrated, two-dimensional flow and transport model, BreZo,[28,29] was used to simulate the

conservative transport of PFOA in the Ohio River from the Washington Works Plant's primary aqueous discharging pipe (outfall 005). The model assumes that PFOA mixes quickly in the vertical direction, which is a reasonable assumption for neutrally buoyant releases into wide rivers, and predicts depth-integrated PFOA concentrations along the length and width of the river downstream of the outfall.[30]

The model was applied to the Ohio River between Parkersburg and New England, WV (about 12 km). The river discharge was specified at the upstream boundary, and the river stage was specified at the downstream boundary, based on annual average rates reported for the United States Geological Survey (USGS) Sewickley Gauging Station in Pennsylvania.[31] The outfall 005 was modeled with a point source in the model domain characterized by a flow rate Q_o and PFOA concentration C_o, which give the mass loading rate as $M_o = Q_o C_o$. Loading rates were specified based on annual Ohio River discharge rates reported by Paustenbach et al.[6] Using annual average river data and loading data, the model predicts annual average PFOA concentrations in river water downstream of the outfall.

Groundwater Flow and Transport Model. Because drinking water was an important source of exposure,[12,14,18] we also developed groundwater flow and transport models, which were not included in the Paustenbach study,[6] to simulate PFOA movement in the saturated groundwater aquifer. The USGS Modular Three-Dimensional Groundwater Flow Model (MODFLOW) was used to calculate hydraulic head.[32] The groundwater flow model using MODFLOW that was developed by DuPont was augmented with a groundwater transport model, MT3DMS.[33] The model consisted of three layers for the representation of different geologic units. Bedrock aquifer was assigned to layer three, the lowest level, while alluvial aquifer for the Ohio River was assigned to layers one and two. All pumping wells including industrial and municipal pumping wells were assigned to layer two, which is the lower layer of the alluvial aquifer.[32] There are multiple wells per each water district for a total of 25, each of which was modeled at its actual geographic location. Pumping rates (m^3/d) for each municipal water supply were calculated from the total daily flows in 2002. Due to limited pumping rate information, historical pumping rates were calculated by assuming that they were proportional to 2002 pumping rates using the ratio of historical pipe length to 2002 pipe length constructed within each water district. The pumping rate for each municipal water supply was assigned to all individual wells within the water district. The wells for the General Electric (GE) Company located along the Ohio River were also included in the model because it serves as a sink for PFOA in the saturated zone. Because annual production information was unavailable for GE Company, we were unable to correlate pumping rates to output from the facilities. Thus, because pumping rates were not available, DuPont and GE pumping rates estimated from limited well information provided by DuPont and GE were also assumed to be constant during the simulation period (1951 - 2008). Hydraulic conductivity and the recharge rate used in the model were obtained from the DuPont groundwater flow model report, which included a calibration that involved comparison of modeled and measured groundwater elevations under the condition of active pumping.[32]

The Modular 3-Dimensional Multispecies Transport Model (MT3DMS) was used to simulate advection, dispersion, and chemical reactions of contaminants in groundwater systems.[33] Groundwater fluxes calculated by MODFLOW were used as input to the MT3DMS model, which used the fluxes to calculate advective transport of PFOA. PFOA was introduced to the transport simulations as variable concentration boundary conditions at the water table surface and along the length of the Ohio River. These boundary conditions were defined using the direct predictions from PRZM-3 and BreZo, with a uniform PFOA concentration applied to each cell accompanying the recharge flux specified in the transport model. Because air deposition and surface water contamination are dependent on short-term releases, these predictions are independent of releases from prior years. In contrast, the concentrations in the soil column and groundwater are influenced by long-term releases, which are reflected in predicted soil and groundwater concentrations from prior years. For this reason, the concentration from the final step of the preceding run was used in the following run as the beginning concentration in the groundwater transport model (MT3DMS) as well as the vadose zone model (PRZM-3). The final output for the linked environmental fate and transport models is PFOA water concentrations for each well in the six municipal water supplies.

Data Sources. Annual PFOA emission rates for air and the Ohio River for the period of 1951 - 2003 were obtained from Paustenbach et al. who reviewed annual purchasing records from the plant and performed material mass balance.[6] Total emission estimates for 2004 - 2006 were provided by DuPont;[16] emission reductions reported for those years were assumed to apply proportionally to each stack. We assumed that all manufacturing processes operated in 2003 were in operation throughout 2008, and assigned the low 2006 emission rate for the years of 2007 and 2008. Figure S1 in the Supporting Information shows the resulting emission estimates for each year.

Because each of the model components requires a different input format, and the model components require substantial communication in each year of simulation from 1951 to 2008 (e.g., annual outputs from PRZM-3 serve as annual inputs to MODFLOW and MT3DMS), extensive data processing is required to link the model components and produce grid predictions over a large time scale. MATLAB (Mathworks, Natick, MA) was used to read and convert output from one model and to assign and write input for others. Most of our MATLAB code was newly written, and we replaced many input files as described previously. Sources of data input and example parameters for each model component are summarized in the Supporting Information, Table S1.

Extensive environmental sampling data were collected within the study area from 1998 to 2008 by DuPont under a Memorandum of Understanding (MOU) with the U.S. Environmental Protection Agency (EPA).[16] These sampling data, mostly collected after 1998, include approximately 8700 measurements of PFOA in public and private well water, 1100 soil concentration measurements, and 2400 air samples. However, few environmental PFOA water measurements are available prior to 1990, when many people were exposed. The analytical method used prior to 1990 involves conversion of all organic fluorine compounds to hydrogen fluoride (HF) and subsequent determination of HF.[34] Therefore, the method is biased high; PFOA is not the only fluorine-containing species converted to HF by this workup. Further, laboratory notes from the analysis suggest low surrogate recoveries (in the 30 - 60% range) with large variability from batch to batch and for surrogates within the same batch. Finally, the data are sparse with as few as one or two data points across the region in a given year. These sparse data show substantial temporal variability calling into question their use to estimate water concentrations. Because of the lack of comparability in methods,

data quality concerns, and the temporal and geographic sparseness of the data, we have opted not to use the data collected prior to 1990 in calibrating the modeling system.

Model Optimization and Calibration. Because of the extensive computational requirements of the model (about a week per run, using a small computing cluster), it is impractical to perform a full multiparameter optimization. Instead we identified the PFOA soil-water partition coefficient (K_d) for a more limited optimization, as it is an influential and highly uncertain parameter driving transport times in the vadose zone and groundwater aquifers. K_d is also the product of the organic carbon partition coefficient (K_{oc}) and the fraction of organic carbon in the soil (f_{oc}). Published estimates for the log K_{oc} vary widely, from 0.79 to 5.84.[35-38] The values of f_{oc} may vary spatially and across water districts, but little information is available on f_{oc} in this region. We applied the constant value of f_{oc} = 0.006 and f_{oc} = 0.002 recommended by EPA for surface and subsurface soil in our model, respectively.[39] The K_d can also be estimated from the octanol-water partition coefficient (K_{ow}), but literature values for the log K_{ow} of PFOA are also widely variable ranging from 2.1 to 6.3.[6,40-42] These large ranges in estimates for K_{oc} and K_{ow} are indicative of experimental difficulties due to the surfactant nature of PFOA.[43]

We conducted a limited single-parameter optimization of K_{oc}, varying it in our model runs, to determine the value providing the best agreement between our model predictions and observed PFOA well water concentrations for the six municipal water districts. Eight different values of K_{oc} were investigated including our initial estimate of 81 L/kg;[38] the final optimal value was selected based on minimizing the following objective function

$$\sum_{j=1}^{X} \left[\log \hat{\phi}_j\right]^2$$

where ϕ_j is the least-squares estimate (LSE) of the ratio between the observed and predicted water concentrations within each water district j. Formally, ϕ_j was estimated by minimizing the following function

$$\sum_{i=1}^{X} \left[\phi_j C_{pred,j} - C_{obs,i,j}\right]^2$$

where $C_{obs,i,j}$ is observed water PFOA concentration for sample i taken from any pumping wells in a water supply j and $C_{pred,j}$ is the corresponding prediction of the water PFOA concentration in a water district j from our linked fate and transport models. This approach has several important implications: (1) within any one water district, each water sample is given equal weight, and differences between observed and predicted values are penalized on an arithmetic scale; (2) each water district is given equal weight in optimizing the K_{oc} regardless of the number of water measurements, with penalties assigned on a log scale; (3) the LSE estimates of ϕ_j may be retained and used to calibrate the model predictions.

RESULTS AND DISCUSSION

Calibration coefficients ϕ_1, ϕ_2, ..., ϕ_7 for each of the eight values of log K_{oc} are shown in Table S4. Calibrated predictions and observed PFOA concentrations (ppb) in log 10 scale for the six municipal water supply wells are shown in Figure 2, using the optimal log K_{oc} value (0.4 L/kg) and corresponding calibration
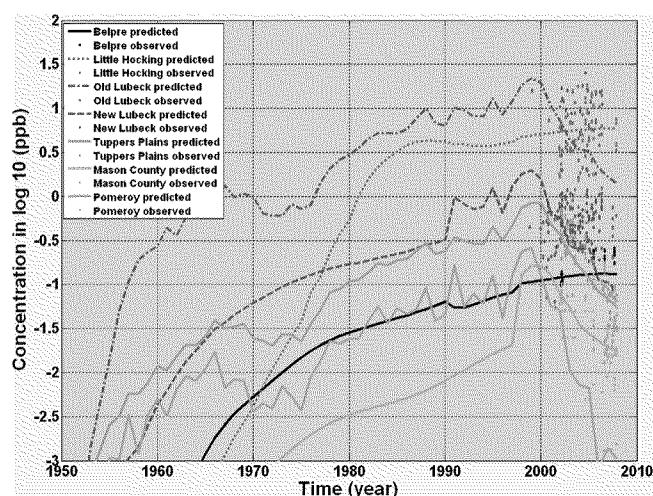

Figure 2. Annual average concentrations (ppb) in log 10 scale in six municipal water supply wells. Calibrated predicted concentrations are shown as lines, and observed concentrations are shown as points.

coefficients from Table S4. Contemporaneously measured groundwater samples from the same municipal water district vary from 1 to 2 orders of magnitude depending on the well location and pumping rate. For example, a Tuppers Plains well closer to the Ohio River pumps more contaminated water compared to a Tuppers Plains well further away that would pump more water diluted by clean rainfall recharge. Lubeck Public Service District concentrations are separated into old and new wells (presented by different lines) because Lubeck moved its well location from the DuPont property to about 3 miles downstream from the DuPont facility in 1991. All predicted groundwater concentrations from the linked air-soil-river-groundwater model pass through most of the measured samples taken from 2000 to 2007 except for old Lubeck. The calibrated predictions for old Lubeck are heavily influenced by four low measurements in 1998; exclusion of these points would have changed the calibration coefficient from 2.1 to 2.6. The Spearman's rank correlation coefficient for predicted versus observed water concentrations is 0.87 after applying the calibration factors (0.86 prior to calibration).

We compared our annual average predicted groundwater concentrations to results from the Paustenbach et al. study[6] for two highly contaminated municipal water supplies, Little Hocking and Lubeck (see Supporting Information, Figure S2). Points are observed concentrations on the log 10 scale, and solid lines and dotted lines are predicted annual average concentrations from Paustenbach et al. and from our model, respectively. Municipal well water concentrations from the Paustenbach et al. study were overpredicted compared to observed concentrations, while predicted concentrations from our calibrated models passed through a cluster of observed concentrations taken from 2000 to 2007. Predicted water concentrations for the Lubeck water district are shown separately for the older (1960-1990) and newer (1991-2008) well locations. Our newly developed groundwater transport model improved the prediction of historical groundwater concentrations by accounting for the transit time in the saturated aquifer, as shown in Figure S2 of the Supporting Information. Our model predictions over time were smoother than those of Paustenbach et al. due to differences in soil depth used in our vadose zone model and the inclusion of a

groundwater transport component which dilutes the effect of annual variations in air deposition. The Paustenbach groundwater prediction for Little Hocking is the result of the vertical transport of deposited PFOA through the vadose zone from PRZM-3 without considering transit time in the saturated zone, and that for New Lubeck is the result of the instantaneous complete mixing in the river from the simplified surface water model. The Paustenbach model predictions ended in 2003 without the advantage of many groundwater concentration measurements and now appear to be overpredicted compared to our model predictions and observed concentrations.

There are dozens of parameters required for each environmental fate and transport model. The K_{oc} value is a paramount parameter, due to its uncertainty and influence on the water concentration predictions. Because the K_{oc} is not used in the air model (AERMOD) or surface water model (BreZo), its optimization only affected the linked vadose zone (PRZM-3) and groundwater (MT3DMS) models. The optimized log K_{oc} for all six municipal water supply wells from the model optimization was 0.40 [L/kg]. This is about a factor of 2 lower than minimum experimental values of 0.79 reported in the literature,[35-38] but comparison with other values is complicated by lack of data on the f_{oc} value in unsaturated and saturated zone; accurate estimation of the K_{oc} using the observed water concentrations is contingent on correct characterization of the f_{oc} and all other model parameters.

After optimization of the K_{oc} but before applying the calibration coefficients, mean predicted water concentrations were within a factor of 2.1 of the mean observed water concentration for each of the six municipal water districts. The calibration constants (φ) for Belpre, Little Hocking, old Lubeck, new Lubeck, Tuppers Plains, Mason County, and Pomeroy were 1.35, 2.00, 2.10, 1.65, 2.00, 0.55, and 0.70, respectively. The range of calibration constants among water districts is likely due to different modeling approaches and unique geographical well locations.

An important limitation in our model prediction is that many environmental measurements are determined by short-term transport, but only annualized PFOA emission rate estimates are available. In fact, hourly and daily emissions are likely to fluctuate substantially depending on the processes being run at the facility. For example, surface soil concentrations and 24 h air concentrations are heavily influenced by recent emission and particle size distributions that may also vary over time. Measured PFOA river water concentrations also heavily depend on the daily emission rate and flow rate. Therefore, we decided that we would only use groundwater concentrations for model optimization, as these measurements are least likely to be influenced by variations in short-term emission rates.

Because substantial air PFOA emissions from the facility continued until about 2006 and vertical vadose zone transit and horizontal groundwater transit are slow processes, untreated public well water near the Washington Works facility may remain contaminated for another decade. Although transit times vary spatially in our models, rough approximations can be obtained using one-dimensional transport models. For example, the mean vertical transit time through the vadose zone is estimated to be 11 years for Little Hocking using our optimized K_{oc} value and 580 cm of soil depth as inputs for the PRZM-3 model.[44] When a higher value of K_{oc} reported in the literature is used in the model, the estimated transit time is even longer.

We also found that the pumping rate of public water wells strongly impacted predictions of groundwater concentrations, but we did not have good data on pumping rates, introducing an important component of uncertainty in our model. For example, an alternative analysis reducing pumping rates in new Lubeck wells by 20% resulted in a noticeably improved fit to measured data for that water district. However, because model predictions are also influenced by many parameters that vary across water districts, we decided to apply linear calibration factors rather than adjusting specific model parameters at the water district level.

Moreover, there are uncertainties regarding the particle size distribution, another influential model parameter, because these data were collected only at one time point during one production process after DuPont installed scrubbers to reduce air emission in 1996. Thus, using particle size distribution after being filtered by scrubbers could induce uncertainties in estimating deposition prior to 1996.[6] Because of uncertainties regarding many of the fate and transport model parameters, it is sensible to calibrate model predictions using the many water PFOA measurements available in recent years. We had once hoped to conduct a Bayesian model optimization, simultaneously adjusting all model input parameters based on the observed water concentrations and subjective prior distributions.[45] However, Monte Carlo approaches are infeasible here due to long run times (several days per iteration). Instead we decided to apply a single linear calibration constant to each water district across all years, after first optimizing the K_{oc} value. This approach takes advantage of the extensive recent water concentration data to scale the predictions, while retaining the shape of each prediction curve generated by the linked fate and transport model.

Some private water wells surrounding the DuPont facility are contaminated with PFOA, probably through percolation of deposited PFOA through the soil after surface deposition. Private well predictions are not included in our model optimization and calibration because critical information including well depth is not available, because observed private well concentrations vary over 3 orders of magnitude within the cluster of private wells, and because few measurements are available for each well.

In addition to air emissions and discharge to the Ohio River, DuPont also disposed of PFOA in their landfills as shown in Figure 1. Detailed information on these landfills including uses, cap system, and history can be found in the DuPont data assessment report.[16] The seepage from landfill to the local groundwater aquifer is not included because past and present contribution from landfill leaching to major public water supplies appears to be negligible based on our groundwater flow and transport model as well as the monitoring data.[16]

Despite the uncertain inputs and parameters, preliminary comparisons with limited sampling data taken from 2000 to 2007 suggest that the predicted water concentrations in public well water systems are the correct order of magnitude and often provide very good approximations to average observed concentrations. Our predicted PFOA groundwater concentrations will be useful for epidemiologic studies that depend on retrospective exposure estimates. Our multicompartment model can be used as a predictive tool for understanding likely patterns of contamination in this region in future years. Model predictions might be improved with more attention to the most influential and uncertain parameters including historical water pumping rates, PFOA particle size distributions, and the PFOA soil - water partition coefficient.

' ASSOCIATED CONTENT

ⓑ Supporting Information. Additional sources of data input and parameters, particle size distributions used by Paustenbach and

Shin, a figure of estimated historical PFOA releases into the study area, and comparison of observed and predicted PFOA concentration by Paustenbach and Shin. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*Phone 949.648.1614; fax 949.824.9863; e-mail hyeongs@uci.edu.

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